



Letter to the Editor

SQUID magnetometry combined with in situ cyclic voltammetry: A case study of tunable magnetism of γ -Fe₂O₃ nanoparticlesStefan Topolovec^{a,*}, Peter Jerabek^b, Dorothée Vinga Szabó^c, Heinz Krenn^b, Roland Würschum^a^a Institute of Materials Physics, Graz University of Technology, Petersgasse 16, 8010 Graz, Austria^b Institute of Physics, University of Graz, Universitätsplatz 5, 8010 Graz, Austria^c Institute for Applied Materials—Materials Processing Technology, Karlsruhe Institute of Technology, P.O. Box 3640, 76021 Karlsruhe, Germany

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ABSTRACT

SQUID magnetometry combined with in situ cyclic voltammetry by means of a three-electrode chemical cell opens up novel potentials for studying correlations between electrochemical processes and magnetic behaviour. The combination of these methods shows that the charge-induced variation of the magnetic moment of nanocrystalline maghemite (γ -Fe₂O₃) of about 4% strongly depends on the voltage regime of charging. Upon positive charging, the charge-induced variation of the magnetic moment is suppressed due to adsorption layers. The pronounced charge-sensitivity of the magnetic moment in the regime of negative charging may either be associated with a redox reaction or with charge-induced variations of the magnetic anisotropy or magnetoelastic coupling.

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The combination of magnetism and electrochemistry has attracted considerable attention in the last years. Apart from magneto-electrochemistry, which deals with electrochemistry in the presence of an imposed magnetic field [1], there are two further fields of interest: One is the electrodeposition of magnetic thin films [2]; the other one is concerning the electrochemically charging-induced variations of the magnetic properties of high-surface area nanomaterials [3–8] and magnetic thin films [9,10]. In both cases the impact of the electrochemical processes on the magnetic properties is of pivotal relevance. Therefore, in situ magnetometry techniques which allow to measure the magnetic properties during electrochemical experiments are necessary. In the case of electrodeposition such in situ measurements were performed with the help of magneto-optical Kerr effect [2,11,12] and alternating gradient field magnetometry [2,13]. In situ studies of the charging-induced modification of magnetic properties of materials were performed by magneto-optical Kerr [9] or Faraday effect [10] as well as by magnetometry using extraction magnetometers [3–7] or a SQUID magnetometer [8]. Most of these measurements were performed with electrochemical cells containing only two electrodes [3–6,8,9]. However, such two-electrode set-ups do not allow to record reliable cyclic voltammograms which are necessary for studying the underlying electrochemical processes. Attempts to apply three-electrode

electrochemical cells were scarcely performed so far (extraction magnetometry: [7]; Faraday effect: [10]) and, to the best of our knowledge, in situ cyclic voltammetry has not yet been combined with SQUID magnetometry.

In the present work [14], a three-electrode electrochemical cell has been designed for operation in a commercial state-of-the-art SQUID magnetometer. To demonstrate the functionality of this measuring set-up, we have examined the tunability of the magnetism of γ -Fe₂O₃ nanoparticles. In a previous work we could show that the magnetic moment of γ -Fe₂O₃ nanoparticles can be varied reversibly up to several percent upon electrochemical charging [8]. By means of the three-electrode cell used in the present study detailed information on the correlation between the electrochemical processes and the magnetic behaviour can be derived.

γ -Fe₂O₃ (maghemite) nanoparticles were prepared by microwave plasma synthesis using Fe(CO)₅ as precursor material and a mixture of 80% Ar and 20% O₂ as reaction gas (for details see, e.g., [15]). The typical particle size of γ -Fe₂O₃ nanoparticles obtained with this method is ca. 4 nm [16]. A porous conductive electrode for charging the insulating γ -Fe₂O₃ nanoparticles in an electrolyte was obtained by intermixing the oxide nanoparticles with commercial platinum nanoparticles (particle diameter: 6–10 nm, Chempur GmbH) in a nominal weight ratio of 1:10 in an ultrasonic bath. Afterwards, this mixture was slightly compacted into a cylindrical pellet with a diameter of 3 mm.

In order to record cyclic voltammograms (CVs) of the pellet in situ in a SQUID magnetometer while measuring the magnetic

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moment simultaneously, a three-electrode electrochemical cell was designed which allowed defined in situ control of charging (see sketch in Fig. 1). The γ -Fe₂O₃/Pt-nanocomposite pellet (sample mass: 14.5 mg) served as working electrode; for electric contact Au wire (diameter: 0.1 mm, purity: 99.9%) was wound around the pellet. This working electrode was placed at the bottom of a cylindrical shaped Teflon container (outer diameter: approx. 5.5 mm, height: approx. 18 mm). The bottom zone of this container was electrically isolated from the upper zone by a battery separator membrane. In the middle of the upper zone, another Au wire (diameter: 0.25 mm, purity: 99.9%), wrapped in a battery separator membrane, was positioned as quasi-reference electrode (QRE). As counter electrode served a high surface area carbon cloth contacted with Au wire (diameter: 0.25 mm, purity: 99.9%) and positioned off-axis in the upper part of the container. The container was filled with 1 M KOH as aqueous electrolyte, closed with a Teflon plug and sealed with epoxy resin.

For testing the in situ electrochemical cell and correlating the potential of the Au quasi-reference electrode to the potential of a standard reference electrode, CVs were recorded in two different set-ups. Beside the measuring set-up with the closed three-electrode cell mounted in the SQUID magnetometer, measurements were conducted with the open cell being mounted into a glass vial. In this set-up, a commercial Ag/AgCl (3 M KCl) reference electrode (Metrohm Autolab) situated in the glass vial was used instead of the Au quasi-reference electrode. As in the

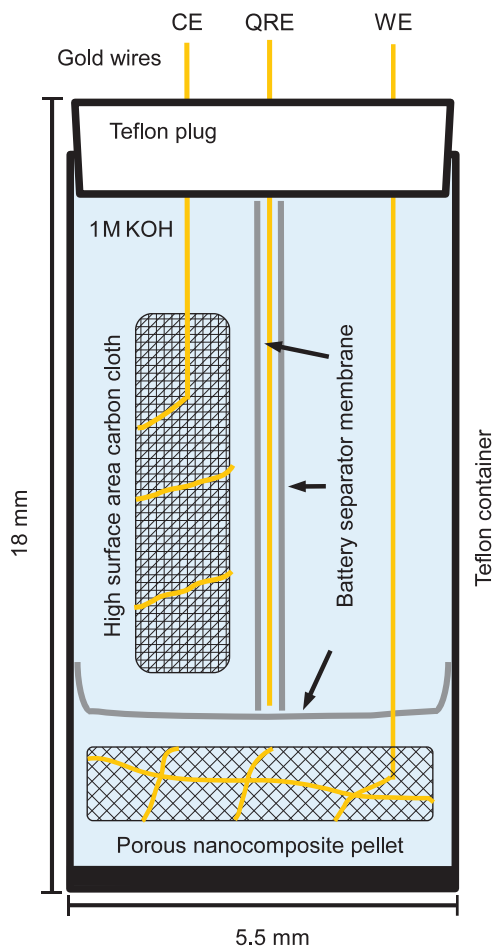


Fig. 1. Scheme of electrochemical cell used for in situ cyclic voltammetry measurements in SQUID magnetometer. WE, QRE, and CE denote working, quasi-reference, and counter electrode, respectively.

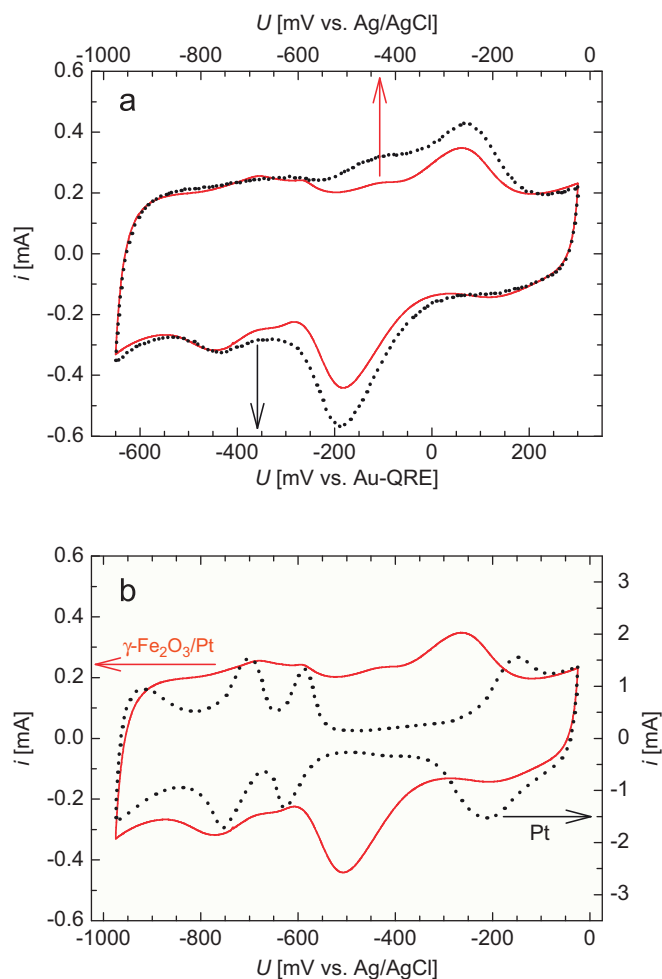


Fig. 2. Cyclic voltammograms (CVs) of nanoporous samples measured with a scan rate of $v = 0.5$ mV/s in 1 M KOH (in each case the last of the three cycles is shown). (a) CVs of the γ -Fe₂O₃/Pt-nanocomposite measured in two different set-ups: in situ electrochemical cell in a SQUID magnetometer at a constant magnetic field of 5 kOe, using Au wire as quasi reference electrode (dotted line); same cell measured ex situ with standard Ag/AgCl reference electrode (solid line). (b) Comparison of the CV of the γ -Fe₂O₃/Pt-nanocomposite (solid line) with that of nanocrystalline Pt (dotted line), both measured with a standard Ag/AgCl reference electrode outside the SQUID magnetometer. The current scales are normalized to the peak currents of the hydrogen adsorption/desorption peaks of Pt.

measurements in the magnetometer, the pellet and the carbon cloth – both situated in the teflon cell – acted as working and counter electrode, respectively. These measurements were performed with an Autolab PGSTAT128N potentiostat (Metrohm Autolab). Unless otherwise stated, the scan rate v used for cyclic voltammetry was 0.5 mV/s and all potential values in the text are given with respect to the Au quasi-reference electrode.

Fig. 2a shows the CVs of the γ -Fe₂O₃/Pt-nanocomposite measured in the two different set-ups (solid line: ex situ with a standard Ag/AgCl reference electrode, dotted line: in situ cell at an applied magnetic field of 5 kOe). Both CVs exhibit the same general shape.¹ This demonstrates that the specially designed in situ electrochemical cell yields reliable CVs. A potential difference of approximately 325 mV between the Au quasi-reference electrode and the Ag/AgCl reference electrode can be deduced from this measurement.

¹ The slightly lower current in the ex situ measurements performed after the in situ measurements may be due to break off of small fragments of the brittle sample pellet or due to exposure to ambient atmosphere during sample transfer.

In Fig. 2b the CV of the γ -Fe₂O₃/Pt-nanocomposite is compared with that of a nanocrystalline Pt reference sample. Both CVs were measured with the Ag/AgCl reference electrode. The reference sample was prepared in the same way as the composite pellet but with Pt nanoparticles exclusively. The CV of the reference sample shows the typical features of a Pt electrode in an aqueous electrolyte [17–19]. The anodic peak at –150 mV vs. Ag/AgCl with the adjoining current plateau and the cathodic peak at –210 mV vs. Ag/AgCl are characteristic for the adsorption and desorption of oxygen species, respectively. At negative potentials ($U < -550$ mV vs. Ag/AgCl), peaks due to hydrogen adsorption and desorption emerge. In the CV of the γ -Fe₂O₃/Pt-nanocomposite an additional broad anodic peak with a maximum at –260 mV vs. Ag/AgCl and a corresponding cathodic peak (–515 mV vs. Ag/AgCl) appear. These two peaks suggest that a reversible electrochemical surface reaction takes place at the γ -Fe₂O₃ nanoparticles and, therefore, will be denoted “maghemite peaks” in the following. At potentials more negative than these maghemite peaks, the relative currents with reference to the peak currents of the hydrogen adsorption/desorption peaks are higher for the composite electrode. Possible reasons for these higher relative currents and the details of the reaction at the maghemite peaks will be discussed later.

For in situ charging of the γ -Fe₂O₃/Pt-nanocomposite pellet in the SQUID magnetometer (MPMS-XL-7, Quantum Design), a PGZ 100 potentiostat (Radiometer Analytical SAS) was used. Simultaneously with the in situ recording the CVs in different potential ranges, the magnetic moment of the γ -Fe₂O₃/Pt-nanocomposite m (including the magnetic moment of the cell) was measured with the SQUID magnetometer. As will be shown later, the magnetic moment of the cell is negligibly small in contrast of the magnetic moment of the γ -Fe₂O₃/Pt-nanocomposite. All measurements were performed for an applied magnetic field of 5 kOe at a temperature of 300 K.

In a first run the potential was cycled several times at a scan rate of $\nu = 0.5$ mV/s between –650 mV and different upper potential limits (–500, –350, 0, +300 mV) and subsequently between +300 mV and different lower potential limits (+150, –150, –500, –650 mV). As shown in Fig. 3 the magnetic moment m varies reversibly upon potential cycling. In the high potential range between +150 and +300 mV a only faint oscillation can be discerned. In agreement with our earlier results [8] the magnetic moment increases with negative charging and decreases with positive charging with extrema close to the potential limits. A slight linear drift is superimposed to the variation of m , the sign and slope of which depend on the scanned potential range. This drift of the magnetic moment might be caused by a

slight shift of the potential of the Au quasi-reference electrode during cycling. The total reversible variation $\Delta m = m_{\max} - m_{\min}$ between the maximum (m_{\max}) and minimum value (m_{\min}) within one cycle after a linear drift correction is dependent on the investigated potential range (see below). The maximum variation of the magnetic moment amounts up to $\Delta m/m_{\min} = 4.2\%$. The good reproducibility and reversibility are demonstrated by the measurements in the potential range between –650 mV and +300 mV which were performed twice (Fig. 3). Irrespective of the potential range studied in advance, the same variation of m is observed in both cases. The magnitude of the m variation of up to 4.2% of γ -Fe₂O₃/Pt-nanocomposite is also in reasonable agreement with our previous measurements on other γ -Fe₂O₃/Pt samples in the two-electrode set-up [8].

The cycling of the magnetic moment in the various voltage ranges (plotted in Fig. 3 as a function of time) is shown in Fig. 4 in more detail along with the cyclic voltammograms monitored simultaneously. The numbers in Fig. 4a and b refer to the sequence in which the CVs were recorded. The nearly perfect overlapping cycles of the magnetic moment (each of the potential ranges was scanned three times), again demonstrates the reversibility of the voltage induced variation of the magnetic moment. Two different regions with strong and weak variation of voltage-induced m become obvious, as indicated by the different slopes in the m – U -plot (Fig. 4c and d). Cycling in potential ranges more negative than the cathodic maghemite peak in the CV (i.e., the cycling sequences 1 and 2 (Fig. 4a)), the variation of m with U is strong, whereas in the potential ranges between –150 mV and +300 mV (cycling sequences 5 and 6), the variation of m with U is low (Fig. 4b and d). Extending the potential range so that the maghemite peaks are crossed during cycling (sequences 3, 4, and 7, 8), the voltage-induced variation of m starts to decrease in the anodic scan (upper m – U branch, Fig. 4c and d) at approximately –50 mV and then rises again at the cathodic scan at approximately –200 mV (lower m – U branch). This shows that the voltage-induced variation of m , i.e., the slope $\Delta m/\Delta U$ of the m – U curves, changes just in the potential region of the maghemite peaks in the CV.

In Fig. 4e and f, the magnetic moment is plotted as a function of the accumulated charge Q , which was obtained by integrating the current of the CVs. From a linear fit of the variation of m with Q a charge coefficient $s_1 = \Delta m/\Delta Q$ of -3.66×10^{-3} emu/C is obtained for the potential range between –650 mV and –350 mV and $s_2 = -0.72 \times 10^{-3}$ emu/C for the range between –150 mV and +300 mV. As for the m – U behaviour, the change of the charge coefficient is related to the maghemite peaks in the CV. On the negative side the absolute value of the charge coefficient is

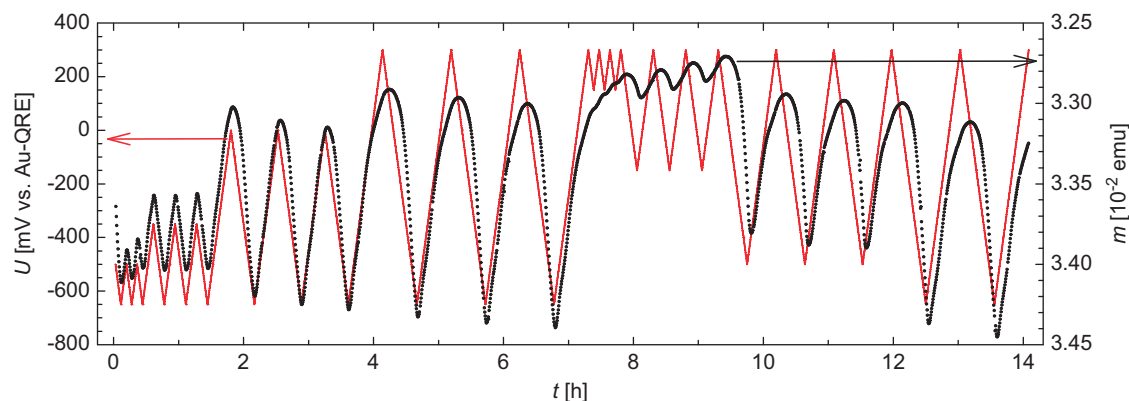


Fig. 3. Variation of the magnetic moment m (dots) of the porous γ -Fe₂O₃/Pt-nanocomposite with time t during electrochemical cycling in different potential ranges between –650 mV and +300 mV at a constant magnetic field of 5 kOe. The potential U (line) was measured versus a Au quasi-reference electrode and cycled with a scan rate of ν of 0.5 mV/s. Note: For better demonstration of the correlation between U and m , the direction of m axis is inverted.

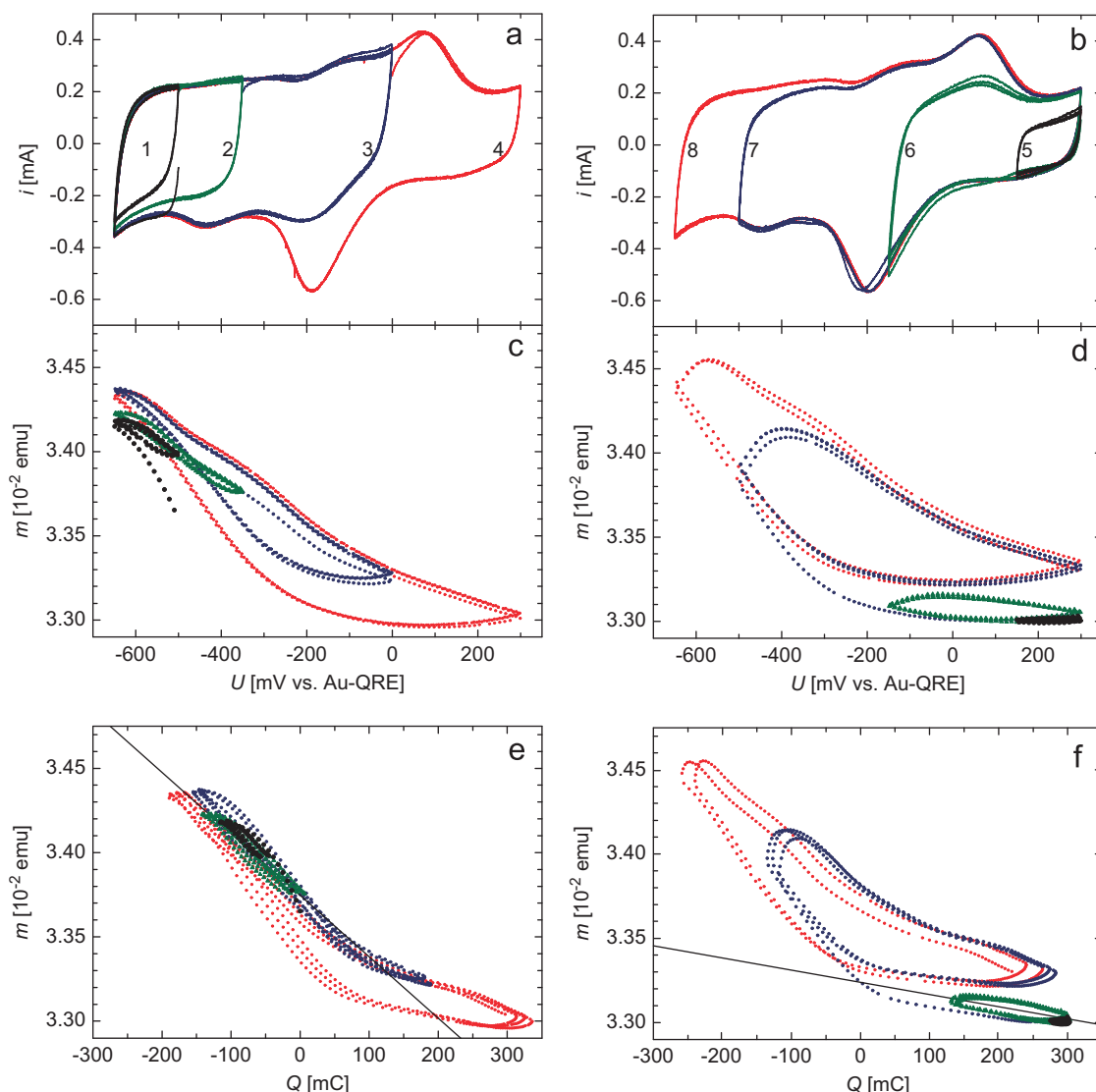


Fig. 4. Combined magnetic and electrochemical measurements of porous γ -Fe₂O₃/Pt-nanocomposite upon in situ charging in 1 M KOH electrolyte with a scan rate of ν of 0.5 mV/s at a constant magnetic field of 5 kOe. (a) and (b) Cyclic voltammograms (CVs) measured in situ in SQUID-magnetometer. The numbers indicate the sequence in which the CVs were recorded. Each potential range was scanned three times (compare Fig. 3). (c) and (d) Magnetic moment m (after linear drift correction) as a function of the applied potential U measured simultaneously with CV. (e) and (f) Plots of m as a function of the accumulated charge Q ((e) belongs to (a, c); (f) to (b, d)). $Q=0$ corresponds to the first data point of m . Linear fits of the m - Q behaviour in the potential range -650 mV to -350 mV (e) and -150 mV to +300 mV (f) are plotted as faint lines visualizing the different slopes in the two charging regions (see text, s_1 , s_2).

by a factor 5 higher compared to the positive side. This indicates that electrochemical reactions of maghemite sensitively affect the tunability of the magnetic moment upon charging.

For studying the influence of scan rates ν , measurements with various ν (in the sequence: 0.5 mV/s, 0.1 mV/s and 1 mV/s) were performed at a fixed potential range between -650 mV and +300 mV. As shown in Fig. 5, the variation of m is rather similar for the different scan rates. The relative variation $\Delta m/m_{\min}$ increases slightly with decreasing ν , which indicates that also a slow electrochemical process may slightly affect the charge-induced variation of m .

To examine whether the charge-induced variation of the magnetic moment is caused by the γ -Fe₂O₃ nanoparticles exclusively or whether interactions between the γ -Fe₂O₃ and Pt nanoparticles play a role, additional measurements were performed on a composite sample of γ -Fe₂O₃ and high surface area carbon cloth. This sample was prepared by dropping 180 μ l of a dispersion (10 mg/ml) of γ -Fe₂O₃ nanoparticles in ethanol on the carbon cloth. For the in situ charging experiments in the SQUID

magnetometer, this composite sample was mounted as working electrode in a two-electrode electrochemical cell as used in our earlier work [8]. Carbon cloth of the same type was used as counter electrode and 1 M KOH as electrolyte. Measurements of m at 50 kOe upon stepwise charging from -850 mV to +850 mV cause reversible variations of m . The magnitude as well as the sign of these variations are in line with the results achieved for the γ -Fe₂O₃/Pt-nanocomposite. This indicates that the reversible variations of m observed for the γ -Fe₂O₃/Pt-nanocomposite are not due to chemical interactions at the γ -Fe₂O₃-Pt interfaces but are exclusively due to charging of the γ -Fe₂O₃ nanoparticles.

Finally, test measurements were performed in order to verify that neither the diamagnetic response of the cell nor the charging current interfere with the magnetic moment detection by the SQUID and that they do not affect the present measurements of the charge-induced variation of m . In order to study the diamagnetic response of the electrochemical cell, SQUID measurements were performed on an electrochemical cell without a γ -Fe₂O₃/Pt-nanocomposite pellet as working electrode. These measurements

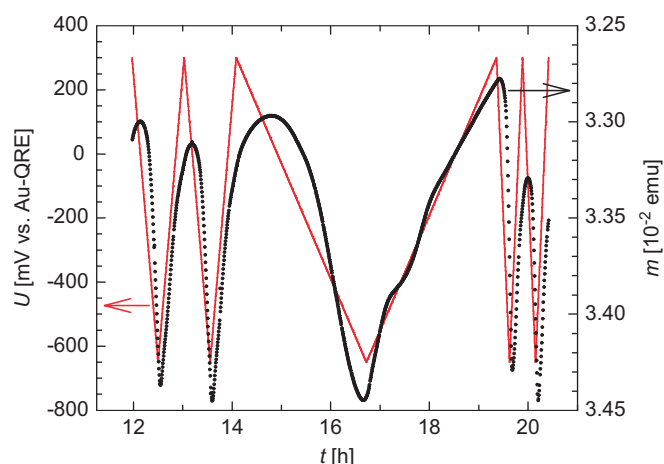


Fig. 5. Variation of the magnetic moment m (dots) of porous γ -Fe₂O₃/Pt-nanocomposite with time t during electrochemical cycling with different scan rates ν (in the sequence: 0.5 mV/s, 0.1 mV/s and 1 mV/s) in the potential range from -650 mV to $+300$ mV at a constant magnetic field of 5 kOe. The potential U (line) was measured versus a Au quasi-reference electrode. The data for $\nu=0.5$ mV/s (left-hand side) are identical to those in Fig. 3 (right-hand side). Note: For better demonstration of the correlation between U and m , the direction of m axis is inverted.

showed that the electrochemical cell has a diamagnetic susceptibility in the order of -10^{-7} emu/Oe. Thus the influence of the cell on the measured magnetic moment is negligibly small. For 5 kOe the magnetic moment of the sample is by a factor of 54 higher than the diamagnetic response of the cell. Even the variation Δm is by a factor of 2.2 larger than the diamagnetic response.

The effect of the current-carrying loop is negligibly small compared to the charging-induced variations of m of the γ -Fe₂O₃/Pt-nanocomposite as outlined in our previous study [8]. The conclusion that the magnetic moment is not influenced by the charging current is further supported by the present measurements performed with the three electrode set-up. As shown in Fig. 4, the variations of m are not directly correlated with the variations of the charging current in the CVs. Furthermore, whereas with increasing scan rate the charging current increases about linearly, the charging-induced variation of m is only scarcely affected by the scan rate (Fig. 5). That is why an appreciable interference of the charging current on the magnetic moment can be excluded.

The present measurements – using nanoscaled γ -Fe₂O₃/Pt as a case study – therefore demonstrate that the three-electrode electrochemical cell can be successfully operated in a state-of-the-art SQUID magnetometer. This opens up novel potentials for studying correlations between electrochemical processes and magnetic behaviour.

As most remarkable features of the present studies in the three-electrode set-up it should be pointed out that the voltage-induced variation of the magnetic moment sensitively depends on the voltage range. The slope $\Delta m/\Delta U$ changes just in the potential region of the maghemite CV peaks. Obviously, the electrochemical reactions, manifested by these CV peaks, are not reflected in discontinuous steps of the magnetic moment of the γ -Fe₂O₃ nanoparticles, but the pronounced m - U variation rather occurs at the negative potential side of these peaks (Fig. 4), even when cycling is entirely limited to this potential range (cycling sequences 1 and 2). This nicely demonstrates the major advantage of using a three-electrode set-up compared to the initial studies in the two-electrode [8] where the charge-induced variation of the magnetic moment could not be unambiguously allocated to the corresponding electrochemical regime.

Although the present letter focuses on the feasibility of the in situ method, an analysis of the underlying electrochemical processes will be given in the following on the basis of literature. The fact that the CV peaks do not directly affect the magnetic moment but the slope $\Delta m/\Delta U$ and the charge coefficient s are hardly compatible with the notion of a reversible transformation of the surface shell between Fe₃O₄ and δ -FeOOH as supposed earlier [8]. Instead, this behavior rather suggests that the peaks are due to the reversible adsorption and desorption of hydroxyl ((OH)⁻) species on the oxide nanoparticles. Indeed, hydroxyl species adsorbed on the γ -Fe₂O₃ nanoparticles at the positive potential side of the maghemite peaks do not change the magnetic moment, but may screen the electrochemical charge. Therefore, this adsorption layer may suppress a charging-induced variation of m in agreement with the low charge coefficient s found in this regime. Upon desorption of the hydroxyl species on the negative potential side of the CV peak, on the other hand, the magnetic behaviour becomes more sensitive to charging as indicated by the substantially higher charge coefficient.

The charging-induced variation of m in this potential regime may either be of electronic or chemical origin. Although there are no further additional peaks assigned to the γ -Fe₂O₃ nanoparticles in the CV, the variation of the magnetic moment upon electrochemical charging could be caused by another redox reaction. Indeed, highly reversible faradaic redox processes may be characterized by pseudocapacitive currents rather than by distinct CV peaks [20]. Such type of a process was found for Fe₃O₄-electrodes by Castro et al. [21]. Among others, the authors considered a continuous transformation of the surface oxide between Fe₃O₄ and γ -Fe₂O₃ caused by a voltage-induced variation of stoichiometry between Fe²⁺ and Fe³⁺ [21]. The relatively high currents at the negative side of the maghemite CV peaks in our measurements may indeed indicate such pseudocapacitive processes. More important, the formation of Fe₃O₄ upon negative charging would be in line with the observed increase of the magnetic moment since Fe₃O₄ exhibits a higher magnetic moment than γ -Fe₂O₃ [22]. Also a consideration of the imposed charge is supporting this view. From the change of the magnetic moment assigned to the reduction of γ -Fe₂O₃ to Fe₃O₄, a necessary charge can be estimated which is by factor of 6 lower than the total imposed charge. A factor of this order appears to be quite reasonable owing to the fact that the major part of the charge is expected to be accumulated on the conductive Pt network.

Alternatively to a chemically induced variation of m , electronic contributions have to be taken into consideration. As shown in recent studies, the magnetic moment of porous nanocrystalline metals [4] and alloys [3,5–7] can be reversibly varied by several percent exclusively by means of capacitive double-layer charging. This variation of m is assigned to a combined effect of charging-induced strain and magnetoelastic coupling [3,5–7]. According to most recent ab initio theoretical studies of a metallic porous nanostructure, charging may also affect the magnetic surface anisotropy and, thus, cause variations of the magnetization of up to several percent [23]. Indication for a electric-field induced variation of the magnetic anisotropy could also derived from density-functional calculations of the surface magnetoelectric effect of ferromagnetic thin metal films [24]. Since for γ -Fe₂O₃, studied in the present work, information on charge-dependences of magnetic surface anisotropy or surface stress is not available, neither of these electronic processes can be excluded.

In conclusion, it should be emphasized that the combination of SQUID magnetometry and in situ cyclic voltammetry, as presented in this work, is not restricted to studies of charge-induced property tuning, but may also be useful for studying elementary processes of electrodeposition of ferromagnetic films as well as complex processes in technological relevant components such as battery materials.

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